PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

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Applicant's or agent's file reference 208925/EP/he	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/EP 03/10923	International filing date *(day/month/year)* 30.09.2003	Priority date *(day/month/year)* 30.09.2002
International Patent Classification (IPC) or both national classification and IPC H01J37/32		
Applicant FUJI PHOTO FILM B.V. et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 6 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 12 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the opinion
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
14.01.2004	19.01.2005
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Weisser, W Telephone No. +49 89 2399-2613

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP 03/10923

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:

Description, Pages

1-9, 12-15, 17-23, 25	as originally filed
10, 11, 11a, 16, 16a, 24	received on 29.12.2004 with letter of 28.12.2004

Claims, Numbers

1-46	received on 29.12.2004 with letter of 28.12.2004

Drawings, Sheets

1/6-6/6	as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).

   ☐ the language of publication of the international application (under Rule 48.3(b)).

   ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   ☐ contained in the international application in written form.

   ☐ filed together with the international application in computer readable form.

   ☐ furnished subsequently to this Authority in written form.

   ☐ furnished subsequently to this Authority in computer readable form.

   ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   ☐ the description, pages:

   ☐ the claims, Nos.:

   ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-27, 29, 45
	No:	Claims	28, 30-44, 46
Inventive step (IS)	Yes:	Claims	1-27
	No:	Claims	28-46
Industrial applicability (IA)	Yes:	Claims	1-46
	No:	Claims	-

2. Citations and explanations

   see separate sheet

1. In this IPER the following documents will be referred to:

   D1: US-A-5 585 147 (OGAWA SATORU ET AL) 17 December 1996 (1996-12-17)
   D2: US-A-5 414 324 (ROTH JOHN R ET AL) 9 May 1995 (1995-05-09)
   D3: PATENT ABSTRACTS OF JAPAN vol. 1999, no. 04, 30 April 1999 (1999-04-30) & JP 11 005857 A (KONICA CORP), 12 January 1999 (1999-01-12)
   D4: EP-A-0 821 273 (EASTMAN KODAK CO) 28 January 1998 (1998-01-28)
   D5: WO 02/23960 A (SIGMA TECHNOLOGIES INTERNATION) 21 March 2002 (2002-03-21)

2. Clarity (Art. 6 PCT)

The frequency range defined in dependent claim 36 (50kHz-1MHz) is not in conformity with the frequency range defined in claim 28 (at least 100kHz) (Art.6 PCT).

3. Novelty (Art. 33.2 PCT)

3.1 None of D1-D5 discloses a method of treating a substrate using an atmospheric pressure glow discharge plasma as defined in the preamble of present claim 1, characterised in that said method comprises a step of controlling the AC-voltage amplitude (applied to the electrodes) above the breakdown voltage.

The subject matter of claim 1 and dependent claims 2-27 is therefore new (Art. 33.2 PCT).

3.2 Any of D1 (cf. Fig.1; col.3-6; examples 11, 14 and 15), D2 (cf. Fig.1; col.3, line 31 - col.4, line 19) and D3 (cf. abstract and Figs.) discloses an arrangement for treating a substrate using an atmospheric pressure glow discharge plasma (APG), comprising
- a plurality of electrodes arranged such that a discharge space is defined by said electrodes,
- means for applying an AC-voltage to said electrodes for generating said plasma,
- means for providing a gaseous substance to said discharge space,
said means for applying an AC-voltage to said electrodes having an amplitude equal to at least a breakdown voltage of said gaseous substance and having a frequency of at least 100kHz (D1: 50Hz-13.56MHz (e.g. 500kHz, 5MHz, 10MHz); D2: 1-100kHz, e.g.

100kHz (explicitly mentioned e.g. in Tab.4,5); D3: 1-100kHz)
and said means for providing a gaseous substance to said electrodes are arranged for essentially providing at least one of a group comprising argon, nitrogen and air (D1: argon; D2: air; D3: argon).
In the arrangement of D2 the AC-voltage amplitude of the means (=AC-power supply) for applying an AC-voltage to said electrodes is adjustable (cf. col.3, line 65). Further, it is evident, though not mentioned in D1 and D3, that the AC-voltage amplitude of the means (=AC-power supply) for applying an AC-voltage to said electrodes of D1 and D3 is also adjustable.
Thereby, in any of D1-D3, the means for applying an AC-voltage to said electrodes appear to be arranged for controlling said AC-voltage amplitude above said breakdown voltage (even if none of D1-D3 discloses the step of controlling said AC-voltage amplitude (as stated in item 3.1 above)).

Therefore, the subject matter of claim 28 appears not to be new (Art. 33.2 PCT).

3.3 The subject matter defined in dependent claims 30-44 and 46 appears also not to be new with regard to D1-D3, as one can immediately see from the citations as indicated in item 3.2 above.

With regard to claim 31 it appears that in any of D1-D3, even though in the method of plasma generating of D1-D3 the concentration of the further (reaction) gas is not stepwisely increased after the plasma has been stabilized, the concentration of the further (reaction) gas is nevertheless stepwise adjustable (by e.g. simply adjusting the outlet control/regulator of the gas bomb).

4. Inventive step (Art. 33.3 PCT)

4.1 None of D1-D5 suggests or provides an incentive to control the AC-voltage amplitude above said breakdown voltage.

The subject matter of claim 1 and dependent claims 2-27 therefore appears to be inventive (Art. 33.3 PCT).

4.2 The subject matter defined in dependent claims 29 and 45 does not appear to involve an

inventive activity (Art.33.3 PCT).

It is not indicated in D1-D3 whether or not the AC-voltage amplitude is less than or equal to approximately 140% of the breakdown voltage. It however appears to be obvious to the skilled person to set the AC-voltage not much higher than necessary to maintain the discharge, i.e. only some 10% higher than the breakdown voltage. It therefore appears not to be inventive to select an AC-voltage in the range 100-140% (or 110-120%) of the breakdown voltage.

Regarding claim 45 it appears to be known in the art that it is advantageous to stabilise the plasma by means of a current choke coil.

5. Industrial applicability (Art. 33.4 PCT)

The subject matter of present claims 1-46 appears to be industrially applicable (Art. 33.4 PCT).

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Another drawback of the application of helium is that due to the specific weight of helium (0.17 g/l), helium is very volatile. For this reason helium gas will always try to escape through the smallest holes of the arrangement. More countermeasures such as appropriate sealing and a more complex system for the gas injection means are required in arrangements using helium as a reaction gas.

Lastly, helium with an atomic weight of 4 will release a relatively small amount of energy in a collision with the surface to be treated. The use of larger, more heavy particles will exchange larger amounts of energy and will assist in the physical treatment of the surface. Therefore, in applications such as surface activation and etching, helium will not be the most favourite choice.

Further to this, heating of the carrier gas in the discharge space, such as is done in US 5,585,147, is not a preferred option for treating thermoplastic polymer films, such as is done in photo film production industry. The higher temperatures may damage the thermoplastic polymers, for instance due to melting thereof. On the other hand, it has been experienced that the temperature automatically rises to some extend due to energy dissipation.

In Japanese Patent Abstract nr. JP 11005857 describes a method of generating a plasma at atmospheric pressure in an ambient filled with 50% by pressure of Argon. The frequency of an AC-voltage used for generating the plasma is kept in between 1 and 100 kHz.

Summary of the Invention

It is an object of the present invention to provide a cost effective method for generating a stable uniform low-temperature atmospheric pressure glow discharge plasma at high operating frequencies of the AC-voltage with outstanding surface treatment capabilities.

These and other objects of the invention are achieved by a

method of treating a substrate using an atmospheric pressure glow discharge plasma (APG), wherein a plurality of electrodes are arranged defining a discharge space for forming said plasma, wherein said electrodes are connected to a power supply and an AC-voltage is applied to said electrodes, and wherein a gaseous substance is provided in said discharge space, wherein said AC-voltage applied to said electrodes has an amplitude equal to at least the breakdown voltage of said gaseous substance and has a frequency of at least 100 kHz, and said gaseous substance essentially comprises at least one of a group comprising argon, nitrogen and air, characterized in that, said method comprises a step of controlling said AC-voltage amplitude above said breakdown voltage for reducing the temperature applied to said substrate for preventing thermal damage to said substrate.

The inventors have discovered that with an AC-voltage of a frequency of 50 kHz and above, by keeping the applied AC-voltage amplitude equal to at least the breakdown voltage (wherein the breakdown voltage is characteristic for each carrier gas used), dissipation of energy can be reduced substantially. Therefore, the temperature in the discharge space may be controlled. Another important finding of keeping the applied AC-voltage at the levels mentioned above is that the uniformity of the generated glow discharge plasma, as it is defined in equation (8), has been significantly improved. A decrease in the minimum exposure time as defined by equation (7) has also been found. The present invention provides thus, a low temperature in the discharge space, a short exposure time and a high level of uniformity of the APG. Hence, this invention can be applied in various process industries including those where thermoplastic polymers are involved having a low glass temperature (T_g), since thermal damage to the thermoplastic polymer can be prevented. As will be appreciated, the applied voltage must be sufficiently large in order to maintain a glow discharge plasma. But it has been found that the amplitude of the applied voltage should not be

too high, at least not higher than 140% of the breakdown voltage of the applied gaseous substance.

In order to further control the temperature in the discharge space, the gaseous substance is kept at a temperature lower than 100°C. Preferably the gas is kept at room temperature, i.e. temperature between 20°C and 30°C.

In the case of a delicate polymer having a low critical

In another aspect of the invention there is provided an arrangement for treating a substrate using an atmospheric pressure glow discharge plasma (APG), comprising a plurality of electrodes arranged such that a discharge space is defined by said electrodes, further comprising means for applying an AC-voltage to said electrodes for generating said plasma, and means for providing a gaseous substance to said discharge space, wherein said means for applying an AC-voltage to said electrodes are arranged for applying an AC-voltage having an amplitude equal to at least a breakdown voltage of said gaseous substance and having a frequency of at least 100 kHz, and said means for providing a gaseous substance to said discharge space are arranged for essentially providing at least one of a group comprising argon, nitrogen and air, characterized in that, said means for applying an AC-voltage to said electrodes are arranged for controlling said AC-voltage amplitude above said breakdown voltage for reducing the temperature applied to said substrate for preventing thermal damage to said substrate.

The above mentioned invention may be applied in various processes in industry, such as in surface activation processes wherein substrate can be glass, polymer, metal, etcetera (specific examples of this are modification of surface properties such as improving adhesion or creating hydrophobic or hydrophilic properties); in the chemical vapour deposition process where specific chemical compositions gasses such as SiH4, hydrocarbons, organosilicons (TEOS, HMDSO, etc.) or organo-metallics are usually involved; in deposition processes of polymers and in deposition processes for oxidic materials; in the surface cleaning processes of various substrates where sterilisation or dry cleaning purposes can be realised. Furthermore the invention may also be excellently applied below atmospheric pressures, such as between 100 mbar and 1 bar (atmospheric pressure).

The present invention will now be further elucidated by description and drawings referring to a preferred embodiment thereof,

directed to the treatment of a substrate service with an APG. The invention is not limited to the embodiments disclosed, which are provided for explanatory purposes.

Brief Description of the Drawings

Fig. 1 is a schematic drawing of an arrangement for

minimum time of exposure t_{minim} 33 are shown.

f [kHz]	P [W]	δD [%]	t_{minim} [s]
129	46	290	63
30	52	120	135
70	89	70	5
282	290	20	9

Example 4

As an example of a measurement at a frequency of approximately 280 kHz, figure 6 presents a diagram of the AC-voltage applied to the electrodes and the plasma current of a plasma generated using a method or arrangement according to the present invention. In this particular example, the carrier gas used was argon at a flow velocity of 2 m/s, the gap distance was 2 mm. The plasma current is shown by the solid line and the applied voltage by the dotted line.

The results of the above-mentioned experiments show a stable APG plasma can be generated in the presence of argon, nitrogen and air at high frequency. However the operation window for maintaining a uniform and stable plasma for the nitrogen and air gasses are rather limited. For argon gas said phenomena is surprisingly not observed. On the other hand, it is observed that at frequency ranges between 200 to 500 kHz, the plasma non-uniformity of the gasses are one order of magnitude smaller than those obtained in the frequency between 1 and 10 kHz. Said observation shows a clear benefit for generating APG plasmas at a higher frequencies, at a frequency of at least 50 kHz. More preferable is a frequency in the range of 100 to 1 MHz, and most preferable in the range of 100 - 700 kHz.

The increased stability of plasma at high frequency is believed to be ascribed to the role of metastables providing the

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CLAIMS

1. Method of treating a substrate (3) using an atmospheric pressure glow discharge plasma (APG) (7), wherein a plurality of electrodes (4,5) are arranged defining a discharge space (10) for forming said plasma (7), wherein said electrodes (4,5) are connected to a power supply (8) and an AC-voltage is applied to said electrodes (4,5), and wherein a gaseous substance (6) is provided in said discharge space (10), wherein said AC-voltage applied to said electrodes (4,5) has an amplitude equal to at least the breakdown voltage of said gaseous substance (6) and has a frequency of at least 100 kHz, and said gaseous substance (6) essentially comprises at least one of a group comprising argon, nitrogen and air, characterized in that, said method comprises a step of controlling said AC-voltage amplitude above said breakdown voltage for reducing the temperature applied to said substrate (3) for preventing thermal damage to said substrate (3).

2. Method according to claim 1, wherein said AC-voltage amplitude is less than or equal to approximately 140% of said breakdown voltage.

3. Method according to claim 2, wherein said AC-voltage amplitude is between 110% and 120% of said breakdown voltage.

4. Method according to any of the previous claims, wherein the temperature of said gaseous substance (6) is lower than 100°C.

5. Method according to any of the previous claims, wherein at least one further gas is provided to said gaseous substance (6) in said discharge space (10).

6. Method according to claim 5, comprising at least the steps of:

providing said further gas to said discharge space (10) after essentially stabilising said plasma (7) such that the concentration of said further gas is fractionally increased stepwise; and

stabilizing said plasma (7) by adjusting said AC-voltage after each stepwise increment of said concentration of said further gas.

7. Method according to any of the claims 5 and 6, wherein said at least one further gas is provided to said gaseous substance (6) in a concentration of at most 50% by volume.

8. Method according to claim 7, wherein said concentration is at most 20% by volume.

9. Method according to any of the claims 5-8, wherein said at least one further gas provided to said gaseous substance (6) in said discharge space (10) is comprised of at least one of a group of O_2, CO_2, NH_3, common precursor gasses such as SiH_4, hydrocarbons, organosilicons such as TEOS and HMDSO, or organo-metallics and combinations thereof.

10. Method according to any of the previous claims, wherein said gaseous substance (6) provided in said discharge space (10) is flowed through said discharge space (10), establishing a gas flow (6).

11. Method according to claim 10, wherein said gas flow (6) has a flow rate in a range of 1 l/min to 50 l/min.

12. Method according to any of the claims 10 and 11, wherein the velocity of the gas flow (6) is in the range of 0.1 - 10 m/s.

13. Method according to claim 12, wherein the velocity of the gas flow (6) is in the range of 1 - 5 m/s.

14. Method according to any of the previous claims, wherein said AC-voltage is chosen to comprise a frequency less than 1 MHz.

15. Method according to claim 14, wherein said frequency of the AC-voltage is chosen within a range of 100 kHz to 700 kHz.

16. Method according to any of the previous claims used for treating a thermoplastic polymer film, wherein a residence time of said thermoplastic polymer film in said discharge space (10) is chosen such that said thermoplastic polymer film is kept at a temperature below said glass transition temperature of said thermoplastic polymer film.

17. Method according to claim 16, wherein said residence time

is controlled by moving said film through said discharge space (10) and controlling the velocity of said film.

18. Method according to any of the previous claims used for treating a thermoplastic polymer film, wherein the amplitude of said AC-voltage is chosen such that the temperature of the discharge space (10) remains below a glass transition temperature of said thermoplastic polymer film during treatment of said film and for maintaining said glow plasma (7).

19. Method according to any of the claims 16-18, wherein said thermoplastic polymer film comprises at least one of a group comprising triacetyl cellulose (TAC), polyethyleneterephthalate (PET), polyethylene-naphthalate (PEN) and similar thermoplastic polymers.

20. Method according to any of the previous claims, wherein at least one of said electrodes (4,5) is covered with a film of dielectric material (2).

21. Method according to claim 20, wherein said film of dielectric material (2) is chosen comprising a thickness in a range of 1 µm to 1000 µm.

22. Method according to claim 21, wherein said thickness lies within a range of 250 µm to 500 µm.

23. Method according to any of the previous claims, wherein at least two of said electrodes (4,5) are spaced apart from each other over a distance within a range of 100 µm to 5000 µm.

24. Method according to claim 23, wherein said distance is chosen within a range of 250 µm to 1500 µm.

25. Method according to any of the previous claims, wherein a voltage rise time defines a shortest time interval for said AC-voltage to reach its maximum value starting from zero, and wherein said voltage rise time of the AC-voltage is in the range of 0.1 to 10 kV/µs.

26. Method according to any of the previous claims, wherein current density through said plasma (7) is kept below 10 mA/cm^2.

27. Method according to any of the previous claims, used for treating a substrate (3) in said discharge space (10) with a chemical vapour deposition process using said plasma (7).

28. Arrangement for treating a substrate (3) using an atmospheric pressure glow discharge plasma (APG) (7), comprising a plurality of electrodes (4,5) arranged such that a discharge space (10) is defined by said electrodes (4,5), further comprising means (8) for applying an AC-voltage to said electrodes (4,5) for generating said plasma (7), and means (19, 21-24, 34) for providing a gaseous substance (6) to said discharge space (10), wherein said means (8) for applying an AC-voltage to said electrodes (4,5) are arranged for applying an AC-voltage having an amplitude equal to at least a breakdown voltage of said gaseous substance (6) and having a frequency of at least 100 kHz, and said means (19, 21-24, 34) for providing a gaseous substance (6) to said discharge space (10) are arranged for essentially providing at least one of a group comprising argon, nitrogen and air, characterized in that, said means (8) for applying an AC-voltage to said electrodes (4,5) are arranged for controlling said AC-voltage amplitude above said breakdown voltage for reducing the temperature applied to said substrate (3) for preventing thermal damage to said substrate (3).

29. Arrangement according to claim 28, wherein said means (8) for applying an AC-voltage are arranged for providing an AC-voltage having amplitude up to 140% of said breakdown voltage.

30. Arrangement according to any of the claims 28 or 29, wherein said means (19, 21-24, 34) for providing a gaseous substance (6) are arranged for providing at least one further gas to said gaseous substance (6) in said discharge space (10).

31. Arrangement according to claim 30, wherein said means (19, 21-24, 34) for providing a gaseous substance (6) are further arranged for providing the at least one further gas such that the concentration of said at least one further gas is stepwise adjustable.

32. Arrangement according to any of the claims 30 or 31, wherein said at least one further gas comprises one of a group of O_2, CO_2, NH_3, common precursor gasses such as SiH_4, hydrocarbons, organosilicons such as TEOS and HMDSO, or organo-metallics and combinations thereof.

33. Arrangement according to any of the claims 28-31, comprising means (17) for flowing said gaseous substance (6) through said discharge space (10).

34. Arrangement according to claim 32, wherein said means (17) for flowing said gaseous substance (6) through said discharge space (10) is arranged for establishing a flow with a flow rate within a range of 1 l/min to 50 l/min.

35. Arrangement according to claim 34, wherein said means (17) for flowing said gaseous substance (6) through said discharge space (10) is arranged for establishing a flow with a flow velocity within a range of

0.1 - 10 m/s.

36. Arrangement according to any of the claims 28-35, wherein said means (8) for applying a high frequency AC-voltage is arranged for applying a voltage comprising a frequency within a range of 50 kHz to 1 MHz.

37. Arrangement according to any of the claims 28-36, wherein at least one of said electrodes (4,5) is arranged for supporting a thermoplastic polymer film to be treated by said plasma (7).

38. Arrangement according to claim 37, further comprising means arranged for moving said thermoplastic polymer film through said discharge space (10) with a velocity for which the residence time of said film is such that the film is kept at a temperature below said glass transition temperature of said thermoplastic polymer film.

39. Arrangement according to any of the claims 37 or 38, wherein said means (8) for applying an AC-voltage are arranged for

providing an AC-voltage having an amplitude such that the temperature of the discharge space (10) remains below a glass transition temperature of said thermoplastic polymer film during treatment of said film.

40. Arrangement according to any of the claims 28-39, comprising a film of dielectric material (2) contiguous to at least one of said electrodes (4,5).

41. Arrangement according to claim 40, wherein said film of dielectric material (2) comprises a thickness in a range of 1 μm to 1000 μm.

42. Arrangement according to any of the claims 28-41, wherein said discharge space (10) comprises dimensions defined by a spacing between said electrodes (4,5) and said dimensions are within a range of 0.1 mm to 5 mm.

43. Arrangement according to any of the claims 28-42, arranged for adjusting the shortest time interval for said AC-voltage to reach its maximum value starting from zero, and wherein said adjusting can be performed at least in a range of 0.1 to 10 kV/μs.

44. Arrangement according to any of the claims 28-43, arranged for adjusting the frequency of said AC-voltage for keeping the current density through said plasma (7) in a range below 10 mA/cm^2.

45. Arrangement according to any of the claims 28-44, comprising a current choke coil arranged for controlling voltage during breakdown.

46. Arrangement according to any of the previous claims, said arrangement being arranged for performing a chemical vapour deposition treatment process on a substrate (3) in said discharge space (10) using said plasma (7).